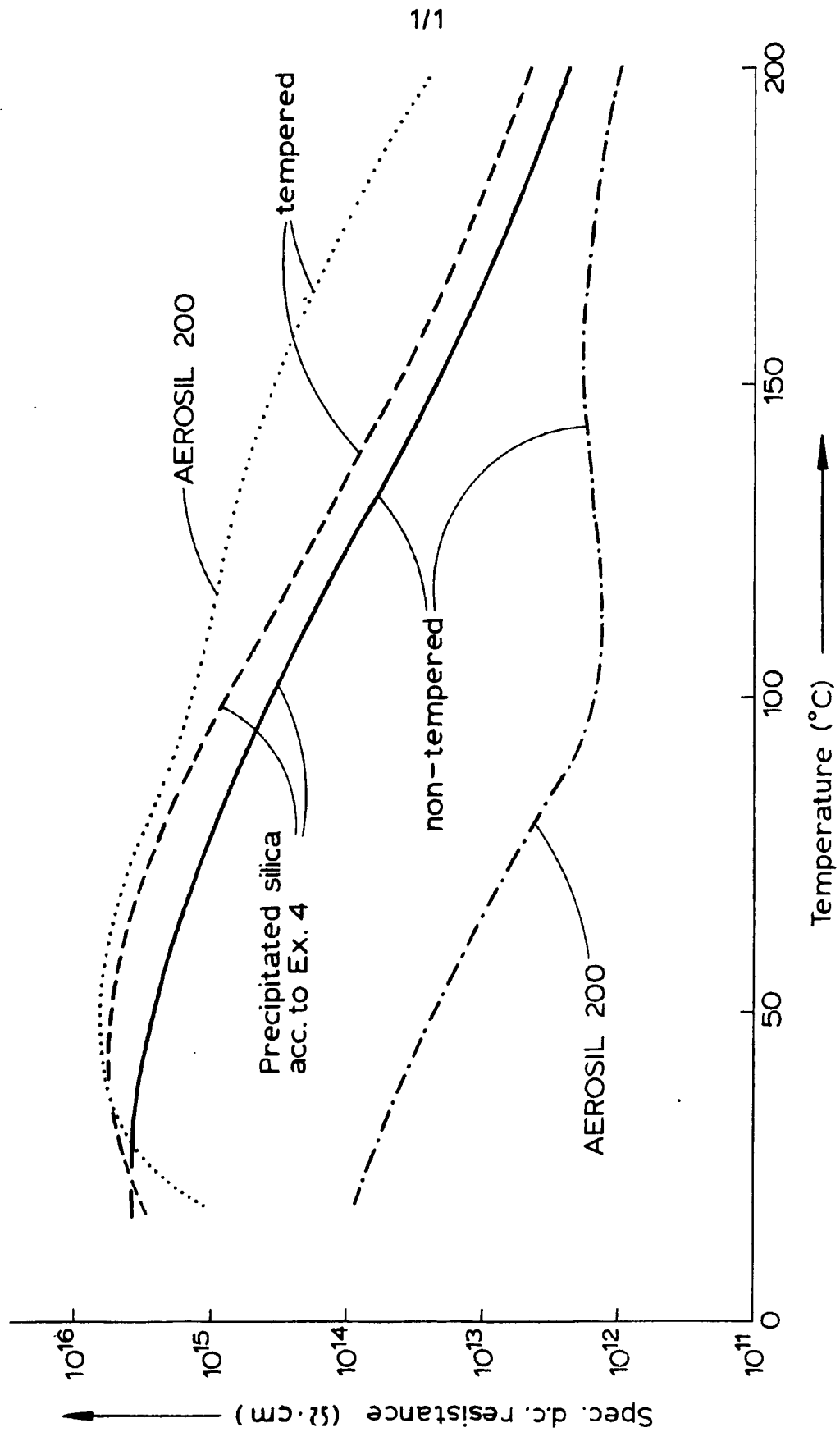


(12) **UK Patent Application** (19) **GB** (11) **2 001 303 A**

(21) Application No 7828256	(54) Hydrophobised Precipitated silica		
(22) Date of filing 29 Jun 1978			
(23) Claims filed 29 Jun 1978	(57) The silica has the following properties:		
(30) Priority data			
(31) 2729244	BET-surface	m ² /g	110±40
(32) 29 Jun 1977			
(33) Fed Rep of Germany (DE)	average primary particles size from		
(43) Application published	EM photographs	nm	15-22
31 Jan 1979			
(51) INT CL ²	drying loss according to DIN 921		
C09C 1/28	after 2 hours at 105°C	%	2.5
(52) Domestic classification	ignition loss (based on the		
C1A 13 310 421 422 423	substance dried for 2 hours at		
510 VF1	105°C) according to DIN 55 921		% 5.5±1.5
(56) Documents cited			
GB 904548	pH-value (in 5 % aqueous-methanolic		
GB 805102	suspension) according to DIN 53 200		7.5±1.0
(58) Field of search			
C1A			
(71) Applicants	conductivity (in 4 % aqueous-methanolic		
Deutsche Gold-und	suspension)	μS	< 600
Silber-Scheideanstalt :			
Vormals Roessler	bulk density of the unventilated		
9 Weissfrauenstrasse,	substance according to DIN 53 194	g/l	130±40
6 Frankfurt Main 1,			
Germany FED. REP.	wettability with water		< 0.1
(72) Inventors			
Peter Nauroth	carbon content	%	2.5±0.6
Heinz Esch			
Robert Huhlmann	water uptake at 30°C % relative		
Rudolf Bode	humidity	%	1.2±0.4
Arthur Reisert			
Harald Bühler			
Günter Türk			
(74) Agents	at 30°C/70 % relative		
Elkington & Fife	humidity	%	1.5±0.5.

A process for the production of such a silica is disclosed. The silica is used as a reinforcing filler in diorganopolysiloxane-based compositions hardenable to form elastomers, particularly in one-component silicon rubber joint-sealing compounds and silicon rubber sheathing compounds.

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SPECIFICATION

Precipitated Silica

5 This invention relates to a hydrophobic precipitated silica and to its use as a reinforcing filler in compositions hardenable to form elastomers.

Fillers are solid substances, generally of inorganic origin and varying in their composition, of which the particles may be fine- to coarse-grained and may vary in shape and which are added to a chemical-technical product in order to improve certain properties.

10 The present invention relates to a hydrophobised precipitated silica which has the following properties: 10

	BET-surface	m ² /g	110 ± 40	
15	average primary particle size from EM photographs	nm	15 - 22	15
	drying loss according to DIN 921 after 2 hours at 105°	%	2.5	
20	ignition loss (based on the substance dried for 2 hours at 105°C) according to DIN 55 921	%	5.5 ± 1.5	20
	pH-value (in 5 % aqueous-methanolic suspension) according to DIN 53 200		7.5 ± 1.0	
	conductivity (in 4 % aqueous-methanolic suspension)	μs	< 600	25
25	bulk density of the unventilated substance according to DIN 53 194	g/l	130 ± 40	
	wettability with water	%	< 0.1	
	carbon content	%	2.5 ± 0.6	
30	water uptake at 30°C/30 % relative humidity	%	1.2 ± 0.4	30
	at 30°C/70 % relative humidity	%	1.5 ± 0.5	

35 In one preferred embodiment of the hydrophobic precipitated silica according to the invention, the drying loss may amount to between 2.5 and 0.0 %. The conductivity of the hydrophobic precipitated silica according to the invention may amount to between 50 and 300 μS. Its wettability with water may amount to between 0 and 0.5.

40 The invention also relates to a process for producing the hydrophobic precipitated silica according to the invention which comprises introducing a hydrophobising agent into an original precipitation suspension of a precipitated silica having the following physical-chemical characteristics (characteristics measured after separation from the precipitation suspension, intensive washing with water and long-term drying of the hydrophilic precipitated silica):

45				45
	BET-surface according to DIN 66 131	m ² /g	160 ± 40	
50	average primary particle size from EM photographs	nm	14 - 22	50
	drying loss according to DIN 55 921 after 2 hours at 105°C	%	2.5 - 4.0	
	ignition loss (based on the substance dried for 2 hours at 105°C) according to DIN 55 921	%	3.5 ± 1.0	
	pH-value (in 5 % aqueous suspension) according to DIN 53 200		7.0 - 8.5	55
55	conductivity (in 4 % aqueous suspension)	μs	< 600	
	bulk density of the unventilated substance according to DIN 53 194	g/l	140 ± 40	
	SO ₃ -content (based on the substance dried for 2 hours at 105°C)	%	0.3	
	Na ₂ O-content (based on the substance dried for 2 hours at 105°C)	%	0.3	60
60				

65 at a pH-value maintained in the alkaline range, stirring the mixture thus obtained separating off the hyd-

rophobised precipitated silica and subjecting it to long-term drying, after which the product obtained is tempered for 60 to 180 minutes and preferably for 70 to 130 minutes at a temperature of from 200 to 400°C and ground.

The original precipitation suspension of the hydrophilic precipitated silica may be obtained as follows:

- 5 1 part by volume of water is introduced into a reaction vessel. 0.15 to 0.25 part by volume of waterglass solution (modules $\text{SiO}_2 : \text{Na}_2\text{O} = 3.5$ and 26 % SiO_2) and 0.015 to 0.025 part by volume of H_2SO_4 (96 % are then slowly added with stirring to the water, an alkaline pH-value being maintained in the mixture during this addition. After the waterglass and H_2SO_4 have been added, the pH-value of the suspension obtained is in the weakly alkaline range.
- 10 The hydrophobising agent used may be an organosilicon compound which is reacted with the hydrophilic precipitated silica suspended in aqueous phase, being of the type hitherto used for a reaction of this nature. It is preferred to use organosilicon compounds corresponding to the general formula



- 15 in which R represents identical or different, monofunctional, optionally substituted and/or polymeric hydrocarbon radicals, $a = 1$ or 2 and Z represents halogen, hydrogen or a radical of the formula $-\text{OH}$, $-\text{OR}$, $-\text{NRX}$, $-\text{ONR}_2$, $-\text{SR}$, $-\text{OOCR}$, $-\text{O}-$, $-\text{N}(\text{X})-$ or $-\text{S}-$, where R is as defined above and X represents hydrogen or has the same meaning as R. Examples of organosilicon compounds such as these are hexamethyl disilazane, trimethyl silane, trimethyl chlorosilane, trimethyl ethoxy silane, triorganosilyl mercaptans, such as trimethyl silyl mercaptan, triorganosilyl acetates, such as vinyl dimethyl acetoxy silane, triorganosilyl amines, such as trimethyl silyl isopropylamine, trimethylsilyl ethylamine, dimethyl phenyl silyl propylamine and vinyl dimethyl silyl butylamine, triorganosilyl aminoxy compounds, such as diethyl aminoxy trimethyl silane and diethyl aminoxy dimethyl phenyl silane, also hexamethyl disiloxane, 1,3-diphenyl tetramethyl disiloxane, 1,3-diphenyl tetramethyl disiloxane and 1,3-diphenyl hexamethyl disilazane.
- 20 Further examples of organosilicon compounds, which may be reacted with hydrophilic precipitated silica suspended in aqueous alkaline phase in accordance with the invention, are dimethyl dichlorosilane, dimethyl ethoxy silane, dimethyl dimethoxy silane, diphenyl diethoxy silane, vinylmethyl dimethoxy silane and octamethyl cyclotetrasiloxane and/or dimethyl polysiloxanes containing from 2 to 12 siloxane units per molecule and 1 Si-conded hydroxyl group in each terminal unit.
- 25 Mixtures of various organosilicon compounds may be reacted with the precipitated silica present in the aqueous original precipitation suspension.
- 30 In one preferred embodiment of the invention, dimethyl dichlorosilane may be used as the hydrophobising agent.

The organosilicon compounds which are reacted with the hydrophilic precipitated silica present in the aqueous alkaline original suspension are preferably used in quantities of from 5 to 30% by weight, based on the weight of the precipitated silica to be reacted with them.

The invention also relates to the use of the hydrophobic precipitated silica according to the invention as a reinforcing filler in diorganopolysiloxane-based compositions hardenable to form elastomers. Thus, in one preferred embodiment, the hydrophobic precipitated silica according to the invention may be used in one-component silicone rubber joint-sealing compounds.

In addition, it may be used in organopolysiloxane elastomers hardenable at room temperature and preferably for example in a two-component silicone compound.

According to the invention, the hydrophobic precipitated silica may be used in hot-vulcanising diorganopolysiloxane elastomers. These elastomers may be used for example as cable insulating compounds.

- 45 Suitable diorganopolysiloxanes are any diorganopolysiloxanes of the type which have hitherto been or could be used as a basis for compositions hardenable or hardening at room temperature (RTV), slightly elevated temperature (LTV) or elevated temperature (HTV) to form organopolysiloxane elastomers. They may be represented for example by the general formula:



- 50 in which R represents identical or different, monofunctional, optionally substituted and/or polymeric hydrocarbon radicals, Z represents a hydroxyl group, a hydrolysable group and/or a hydrolysable atom or, in the case of compositions hardenable at only slightly elevated temperature, alkenyl groups, $n = 1, 2$ or 3 and x is an integer having a value of at least 1.

- 55 Examples of the hydrocarbon radicals R are alkyl radicals, such as methyl, ethyl, propyl, butyl, hexyl and octyl radicals; alkenyl radicals, such as the vinyl, allyl, ethylallyl and butadienyl radical; and aryl radicals, such as the phenyl and tolyl radical.

Examples of substituted hydrocarbon radicals R are in particular halogenated hydrocarbon radicals, such as the 3,3,3-trifluoropropyl radical, the chlorophenyl and the bromotolyl radical; and cyanoalkyl radicals, such as the β -cyanoethyl radical.

Examples of polymeric (or "modifying") substituted and unsubstituted hydrocarbon radicals R are polysilyl, polyvinylacetate, polyacrylate, polymethacrylate and polyacrylonitrile radicals attached to silicon through carbon.

At least the predominant proportion of the radicals R preferably consists of methyl groups, above all by virtue of their easier accessibility. The other radicals R present, if any, are in particular vinyl and/or phenyl

groups.

In the particular case of compositions storable in the absence of water and hardening at room temperature to form elastomers in the presence of water, Z generally represents hydrolysable groups. Examples of

- groups such as these are amino, amido, aminoxy, oxime, alkoxy, alkoxy-alkoxy (for example
 5 $\text{CH}_3\text{OCH}_2\text{CH}_2\text{O}-$) alkenyloxy (for example $\text{H}_2\text{C}=(\text{CH}_3)\text{CO}-$), acyloxy and phosphate groups. Z preferably represents acyloxy groups and, more particularly, acetoxy groups, above all by virtue of their easier accessibility. However, excellent results are also obtained for example where Z represents oxime groups, such as those of the formula $-\text{OH}=\text{C}(\text{CH}_3)(\text{C}_2\text{H}_5)$.

Examples of hydrolysable atoms Z are halogen and hydrogen atoms.

- 10 Examples of alkenyl groups Z are, in particular, vinyl groups.
 Identical or different Z's may be bound to an Si-atom.

Mixtures of various diorganopolysiloxanes may be used.

- Compositions hardenable to form elastomers either at room temperature or at only slightly elevated temperature, optionally after the addition of crosslinking agents, and in particular compositions storable in
 15 the absence of water and hardening to form elastomers at room temperature in the presence of water are produced from the hydrophobic precipitated silica according to the invention by admixture with diorganopolysiloxanes and, optionally, other substances. Mixing may be carried out in known manner, for example in mechanical mixers.

- The fillers used in accordance with the invention are preferably added in quantities of from 5 to 50 % by weight, based on the total weight of the compositions hardenable to form elastomers. In the case of
 20 HTV-organopolysiloxane elastomers, quantities of from 5 to 50 % by weight may be used. In the case of RTV-organopolysiloxane elastomers, quantities of from 5 to 35 % by weight and preferably quantities of from 5 to 25 % by weight may be used.

- Where the diorganopolysiloxanes containing reactive terminal units contain as sole reactive terminal
 25 units those containing Si-bound hydroxyl groups, these diorganopolysiloxanes have to be reacted in known manner with crosslinking agents, optionally in the presence of condensation catalysts, in order to harden them in known manner or to convert them into compounds hardening to form elastomers under the effect of the water present in air, optionally with addition of more water. In the case of HTV-diorganopolysiloxane elastomers, organic peroxides, such as for example bis-2,4-dichlorobenzoyl peroxide, benzoyl peroxide,
 30 dicumyl peroxide, tert.-butyl perbenzoate or tert.-butyl peracetate, may be used as crosslinking agents at correspondingly high temperatures.

- The hot-vulcanising organosiloxanes used may be those of the type whose organic substituents consist of methyl, ethyl, phenyl, trifluoromethyl phenyl $[\text{F}_3\text{CC}_6\text{H}_4-]$ or trimethylsilyl methylene radicals $[(\text{CH}_3)_3\text{SiCH}_2-]$,
 35 for example dimethyl diethyl, phenyl methyl, phenyl ethyl, ethyl methyl, trimethyl silyl methylene methyl, trimethylsilyl methylene ethyl, trifluoromethyl phenyl methyl or trifluoromethyl phenyl ethyl siloxanes or copolymers of these compounds. In addition, the polymers may contain limited quantities of diphenyl siloxane, bis-trimethyl silyl methylene siloxane, bis-trifluoromethyl phenyl siloxane units and also siloxanes containing units of the formulae $\text{RSiO}_{1.5}$ and $\text{R}_2\text{SiO}_{0.5}$ where R represents one of the above radicals.

Examples of crosslinking agents are, in particular, silanes corresponding to the general formula:

- 40 $\text{R}_4\text{SiZ}'_t$,

in which R is as defined above, Z represents a hydrolysable group and/or a hydrolysable atom and $t = 3$ or 4 . The above mentioned examples of hydrolysable groups Z and hydrolysable atoms Z also apply in their full scope to the hydrolysable groups Z' and the hydrolysable atoms Z'.

- 45 Examples of silanes corresponding to the above formula are methyl triacetoxy silanes, isopropyl triacetoxy silane, isopropoxy triacetoxy silane, vinyl triacetoxy silane, methyl-tris- diethylamino-oxy silane, methyl-tris- (cyclohexylamino)- silane, methyl-tris- (diethylphosphato)- silane and methyl-tris- (methylethyl-ketoximo)- silane.

- Instead of, or in admixture with, silanes corresponding to the above formula, it is also possible to use for
 50 example polysiloxanes which contain at least three Z'-groups or atoms per molecule, those silicon valencies which are not saturated by Z'-groups or atoms being saturated by siloxane oxygen atoms and, optionally, R-groups. The most well known examples of crosslinking agents of the latter type are polyethyl silicate with an SiO_2 -content of approximately 40 % by weight, hexaethoxy disiloxane and methyl hydrogen polysiloxanes.

- 55 The most well known examples of condensation catalysts are tin salts of fatty acids, such as dibutyl tin dilaurate, dibutyl tin diacetate and tin (II) octoate.

- Where the diorganopolysiloxanes containing reactive terminal units contain as sole reactive units those comprising alkenyl groups, hardening to form elastomers may be carried out in known manner with organopolysiloxanes which contain on average at least three Si-bound hydrogen atoms per molecule, such as
 60 methyl hydrogen polysiloxane, in the presence of catalysts promoting the addition of alkenyl groups with Si-bound hydrogen, such as chloroplatinic (IV) acid. In this case, the compositions obtained are hardenable either at room temperature or at only slightly elevated temperature (generally 50 to 80°C), i.e. LTV-compositions.

- Finally, hardening by means of polycyclic organopolysiloxanes in the presence of equilibration catalysts,
 65 such as phosphornitrile chlorides, is mentioned as another example of hardening to form elastomers.

- In addition to diorganopolysiloxanes, the precipitated silica according to the invention, crosslinking agents and crosslinking catalyst, the compositions hardenable to form elastomers may of course optionally contain fillers of the type normally or frequently used in compositions hardenable to form elastomers. Examples of substances such as these are fillers having a surface of less than $50 \text{ m}^2/\text{g}$, such as quartz powder, diatomaceous earth, also zirconium silicate and calcium carbonate, untreated pyrogenic silicon dioxide, organic resins, such as polyvinyl chloride powder, organopolysiloxane resins, fibrous fillers, such as asbestos, glass-fibres and organic fibres, pigments, soluble dyes, aromas, corrosion inhibitors, agents stabilising the compositions against the influence of water, such as acetic acid anhydride, agents which delay hardening, such as benzotriazole, and plasticisers such as dimethyl polysiloxane terminally blocked by trimethyl siloxy groups.
- By virtue of the above mentioned combination of physical-chemical characteristics, coupled with its excellent dispersibility, the hydrophobic precipitated silica according to the invention may be used as an extremely effective reinforcing filler. The distinct reduction in the equilibrium moisture content by comparison with known precipitated silicas affords advantages in processing, for example in pressureless vulcanisation in which the vulcanisates obtained contain fewer bubbles by comparison with those obtained using the known, hydrated precipitated silica. Finally, the low electrolyte content coupled with the low moisture content means that the vulcanisates have favourable electrical properties. In cold-hardening silicone rubber sealing compounds, the hydrophobic precipitated silica according to the invention, by virtue of its low water content, affords advantages in regard to the storability of the non-hardened compositions.
- The production, physical-chemical values and use of the hydrophobic precipitated silica according to the invention are illustrated by the following Examples:

EXAMPLE 1

- Production of the original precipitation suspension of a hydrophilic precipitated silica for subsequent wet-hydrophobising:
- 50.0 m³ of water are introduced into a reaction vessel. 9.2 m³ of a waterglass solution and 0.9 m³ H₂SO₄ are slowly added to the water with stirring, an alkaline pH-value being maintained in the mixture during the addition. After the waterglass and H₂SO₄ have been added, the pH-value of the suspension obtained lies in the alkaline range.
- For characterising the hydrophilic precipitated silica, part of the suspension is filtered off, washed until low in electrolyte, subsequently dried at 105°C in a drying cabinet until constant in weight and ground in a pinned-disc mill.
- The hydrophilic precipitated silica obtained has the following physical-chemical characteristics:

BET-surface according to DIN 66 131	m ² /gk	155	
average primary particle size from EM photographs	nm	18 - 20	40
drying loss according to DIN 55 921 after 2 hours at 105°C	%	3.0	
ignition loss (based on the substance dried for 2 hours at 105°C)	%	3.3	
according to DIN 55 921		7.7	
pH-value (in 5 % aqueous suspension) according to DIN 53 200	μs	240	45
conductivity (in 4 % aqueous suspension)	g/l	140	
bulk density of the unventilated substance according to DIN 53 194	%	0.22	
SO ₂ content (based on the substance dried for 2 hours at 105°C)	%	0.18	
Na ₂ O-content (based on the substance dried for 2 hours at 105°C)			50

55 Procedure for determining electrical conductivity

- A 4.0 g sample of silica is heated with 50 ml of fully desalted water in a 150 ml glass beaker and boiled while stirring for 1 minute. The suspension is then transferred to a 100 ml measuring flask, cooled and filled up to the mark with fully desalted water. After shaking, the measuring cell of the conductivity meter is first flushed with the suspension to be measured and then filled with or dipped into the suspension. The electrical conductivity is read off from the meter and the temperature of the suspension determined during the measurement.

Calculation: The electrical conductivity is expressed in μS, based on a temperature of 20°C.

EXAMPLE 2

- Production of a hydrophobic precipitated silica according to the invention obtained by wet-

5

hydrophobising

193 g of dimethyl dichlorosilane are added over a period of 30 minutes with intensive stirring to 10 litres of an aqueous original precipitation suspension of the precipitated silica according to Example 1 with a solid concentration of 57.9 g/l, the pH-value of the suspension being kept at 8.5 during the addition. After subsequent mixing for 60 minutes, the precipitated silica, of which 25 % is coated with dimethyl dichlorosilane, is separated off, dried at 105°C, tempered for 2 hours at 350°C and subsequently ground.

The hydrophobic precipitated silica obtained has the following physical-chemical characteristics:

10		%	5.5	10
	ignition loss at 1000°C according to DIN 55 921			
	of which moisture makes up 0.4 % at 105°C in accordance with DIN 55 921	m ² /g	89	15
15	pH-value according to DIN 66 131	%	0.05	
	wettability with water	μs	160	
	conductivity	%	2.2	
	C-content	%	1.2	20
20	water uptake at 30°C/30 % relative humidity	%	2.0	
	at 30°C/70 % relative humidity	g/l	130	
	bulk density of the unventilated substance according to DIN 53 194			25

25

Determination of the wettability with water of hydrophobic silicas

The determination of the water-wettable fractions of hydrophobic silica is described in the following:

30 *Determination procedure:*

0.2 g of hydrophilic silica are introduced with 50 ml of distilled water into a 250 ml separatory funnel and shaken for 1 minute at maximum speed by means of a Turbula mixer.

After the wetted fractions have been briefly left to settle, 45 ml of the suspension are run off after careful rotation into an evaporating dish, concentrated by evaporation on a water bath and then dried at 105°C.

$$\text{calculation: } \frac{\text{dry residue} \cdot 100}{\text{weight portion}} = \% \text{ water-wettable fractions}$$

40 *Determination of moisture uptake*

Moisture uptake is determined by measuring the maximum or time-dependent moisture uptake of silicas in dependence upon temperature and relative air humidity.

45 *Determination procedure:*

A silica sample weighing approximately 2.5 g is weighed to an accuracy of 0.1 mg into a dry tared weighing glass and dried for 2 hours at 105°C. After cooling, the weight is determined on an analytical balance. The open weighing glass containing the sample is then stored in a conditioning cabinet at a predetermined temperature and relative air humidity level. A moisture uptake time graph may then be recorded or alternatively the maximum moisture uptake may be determined.

Determination is normally carried out at

30°C/30 % relative air humidity

30°C/70 % relative air humidity

$$\text{calculation: } \frac{\text{g weighed out} \cdot 100}{\text{g weighed in} \cdot \text{dried sample}} = \% \text{ moisture uptake}$$

55

EXAMPLE 3

Use of a hydrophobic precipitated silica according to the invention in cold-hardening one-component silicone rubber compositions.

In this Example, the hydrophobic precipitated silica according to the invention of Example 2 is tested as a reinforcing filler and thixotropic agent in a one-component silicone rubber joint-sealing compound (cold-vulcanising).

In the tests, Degussa's silica Aerosil (Registered Trade Mark) 150 and Wacker's commercial product HDK H2000 are tested for comparison in the same silicone rubber composition.

HDK H2000 is a highly disperse silica which is produced by the flame hydrolysis of volatile silicon com-

pounds and subsequently hydrophobised by reaction with organosilanes. Accordingly, it has a dense surface covering of trimethyl silyl groups and shows the following physical-chemical characteristics:

BET-surface	m ² /g	170 ± 30	
5 SiO ₂ -content	% by weight	>97	5
apparent density, unpressed	g/1	approx. 90	
moisture according to DIN 53 198, method A, 2 hours at 105°C	% by weight	<0.6	10
10 ignition loss according to DIN 52 911, 2 hours at 1000°C	% by weight	<2.5	
pH-value according to DIN 53 200 in a 4 % dispersion in water-methanol (1:1)		6.7-7.7	
15 grit according to Mocker (DIN 53 580)	% by weight	<0.05	15
adhering HCl	% by weight	<0.020	
Al ₂ O ₃	% by weight	<0.05	
20 Fe ₂ O ₃	% by weight	<0.005	20
TiO ₂	% by weight	<0.003	
C	% by weight	<3	
			25
25			
			30
30			

Aerosil 150 is a pyrogenic silica having the following physical-chemical characteristics:

			35
35	m ² /g	150 ± 50	
BET-surface	nm	14	
average primary particle size		0.5	
drying loss (DIN 53 198/A) (2 hours at 105°C)		1	40
40 ignition loss (DIN 52 911) (2 hours at 1000°C)		3.6-4.5	
pH-value (DIN 53 200) (in 4 % aqueous dispersion)	%	99.8	
SiO ₂ *	%	0.05	
Al ₂ O ₃	%	0.003	45
45 Fe ₂ O ₃	%	0.03	
TiO ₂	%	0.025	
HCl	%	0.05	
grit according to Mocker (DIN 53 580)		hydrophilic	50
50 wetting behaviour			
			55
55			
			60

60 * based on the substance calcined for 2 hours at 1000°C.

The composition is based on the following recipe with acetate hardener:

68.4 parts by weight of dimethyl polydisiloxane containing terminal hydroxyl groups, viscosity 50,000 cSt.

271 parts by weight of dimethyl polysiloxane containing terminal trimethyl siloxy groups, viscosity 1000

cSt.

65 4.5 parts by weight of methyl triacetoxysilane (crosslinker) 0.005 parts by weight of dibutyl tin diacetate + 65

silica to be tested.

The silica is incorporated following addition of the crosslinker in an evacuable planetary mixer.

The still pasty joint-sealing compound or its vulcanisate hardened in air for 7 days was then subjected to the following test:

- 5 (a) extrudability (ASTM 2452-69)
- (b) staying power (Hutchen method)
- (c) modulus at 100 % elongation (DIN 53 504)
- (d) tensile strength (DIN 53 504)
- (e) elongation at break (DIN 53 504)
- 10 (f) tear propagation resistance (DIN 53 515)
- (g) Shore-A-hardness (DIN 53 505).

The results of these tests are set out in Table I below. They show the following technical advantage over the known pyrogenic hydrophilic silica Aerosil 150 and the hydrophobic silica HDK H2000:

- Aerosil 150 can only be incorporated into the one-component sealing compound in a quantity of up to 8 %.
- 15 Any increase beyond this filling level makes the composition difficult to process. The level of mechanical data obtainable with a filling level of 8 % corresponds to the prior art.
- By contrast, the silica according to the invention of Example 2 used in a quantity corresponding to a filling level of 20 % gives a much higher level of mechanical data which satisfies the requirements of high-strength sealing compounds. Despite this high filling level, the extrudability of the composition is entirely satisfac-
- 20 tory. Its storability is also good.
- By contrast, the level of mechanical data of the commercial product HDK H2000, which represents the latest prior art, for a filling level of 20 % is not comparable with that of the vulcanisates filled with the precipitated silica according to the invention. This applies in particular to tensile strength and elongation at break, both of which are 45 % lower than the corresponding values of the silica according to the invention.
- 25 Only by increasing the filling level to 25 % does the data level of HDK H2000 become fully comparable.
- Accordingly, these findings surprisingly show that, by using only 20 % of the precipitated silica according to the invention, it is possible to obtain a property spectrum which, in some respects, is distinctly better (than 25 % of HDK H2000). In view of the significantly lower production costs by comparison with pyrogenic hydrophobic silica, additional potential applications are opened up in this way.

TABLE I

Testing of a hydrophobic precipitated silica according to the invention of Example 2 against conventional pyrogenic silica in a one-component silicone sealing compound:

Silica		Stability	Staying	Extrudability
Type	(%)*	in storage	power (Hutchen method)	(g/min.)
silica of Example 2	20	good	good	8.2 after 0 days 8.0 after 28 days
Aerosil 150	8	good	good	8 after 0 days 8 after 28 days
HDK H2000	20	good	good	19 after 0 days 22 after 28 days
	25	good	good	11 after 0 days 9 after 28 days

* % by weight, based on the mixture as a whole

Silica		Modulus	Tensile	Elongation	Tear	Shore-
Type	(%)*	100 (N/mm ²)	strength (N/mm)	at break (%)	propagation resistance (N/mm)	A- hardness
silica of Example 2	20	4.6	45	780	16	18
Aerosil 150	8	3.0	10	400	2.5	20
HDK H2000	20	5.0	25	430	15	24
	25	6.0	45	490	18	32

* % by weight, based on the mixture as a whole

EXAMPLE 4

Production of a hydrophobic precipitated silica according to the invention obtained by wet-hydrophobising. 175.6 g of dimethyl dichlorosilane are introduced over a period of 30 minutes with intensive stirring into 12 litres of an original precipitation suspension of the precipitated silica of Example 1 with a solids concentration of 57.9 g/l, the pH-value of the suspension being kept at 8.5 during the addition. After subsequent mixing for 60 minutes, the precipitated silica, of which 20 % is covered with dimethyl dichlorosilane, is dried at 105°C, tempered for 1.5 hours at 350°C and subsequently ground. The precipitated silica obtained has the following physical-chemical characteristics:

15				
	ignition loss at 1000°C (DIN 55 921)	%	5.5	
	of which moisture makes up 0.4 % at 105°C (DIN 55 921)			
	pH-value according to DIN 53 200		7.5	
20	BET-surface according to DIN 66 131	m ² /g	94	20
	wettability with water		0.06	
	conductivity	μs	92	
	C-content	%	2.1	
25	water uptake at 30°C/30 % relative humidity	%	1.3	25
	at 30°C/70 % relative humidity	%	2.0	
	bulk density of the unventilated substance (DIN 53 914)	g/l	137	30
30				

35

EXAMPLE 5

Use of a hydrophobic precipitated silica according to the invention in sheathing compounds based on organopolysiloxanes.

In this Example, the hydrophobic precipitated silica according to the invention of Example 4 is incorporated as a reinforcing filler in hot-vulcanising silicone rubber and the resulting vulcanisates tested for their electrical volume resistance.

By virtue of its excellent dielectric properties, hot-vulcanising silicone rubber is also used as a high-quality cable insulating material. In this case, highly active pyrogenic silica is normally used as reinforcing filler by virtue of its uniformity and favourable dielectric properties. It is known that the insulating properties can be further improved by subjecting the fully vulcanised compositions to a prolonged tempering process (at least 6 hours) at elevated temperatures (of the order of 200°C).

The following recipe was used for the tests associated with this Example:

100 parts by weight of dimethyl polysiloxane containing terminal trimethyl siloxy groups and vinyl groups.
40 parts by weight of silica
2.4 parts by weight of bis-2,4- dichlorobenzoyl peroxide (50 % paste in silicone oil)
vulcanisation : 7 minutes at 130°C
tempering: 0 or 6 h at 200°C
conditioning: 24 hours at 22°C/80 % relative air humidity.

The test results are shown in Figure 1 by comparison with Aerosil 200, a pyrogenic silica manufactured by Degussa. As the curves show, it is surprisingly possible to obtain with the precipitated silica according to the invention resistance values as good as those obtained with the pyrogenic silica. It was also surprisingly found that, with the silica according to the invention, the favourable electrical properties can even be obtained without the above mentioned elaborate tempering process. Apart from the more favourable production costs, this represents another advantage of the precipitated silica according to the invention.

Aerosil 200 is a highly disperse silica produced by the flame hydrolysis of volatile silicon compounds and having the following physical-chemical characteristics:

	BET-surface	m ² /g	200±25	
	average primary particle size	m μ	12	
	bulk density (DIN 53 194)	ml/100 g	1700	
	compacted product	ml/100 g	1000	5
5	drying loss (DIN 53 198/A) 2 hours at 105°C	% by weight	< 1.5	
	ignition loss (DIN 52 911) 2 hours at 1000°C	% by weight	< 1.5	
	pH-value (DIN 53 200) in 4 % aqueous dispersion		3.6-4.3	
	SiO ₂	% by weight	> 99.8	10
10	Al ₂ O ₃	% by weight	< 0.05	
	Fe ₂ O ₃	% by weight	< 0.03	
	TiO ₂	% by weight	< 0.03	
	HC1	% by weight	< 0.025	15
15	grit according to Mocker (DIN 53 580)	% by weight	0.05	

CLAIMS

- 20 1. A hydrophobised precipitated silica having the following properties:
- | | | | | |
|----|---|-------------------|---------|----|
| | BET-surface according to DIN 66 131 | m ² /g | 110±40 | |
| | average primary particle size from EM photographs | nm | 15-22 | |
| | drying loss according to DIN 55 921 after 2 hours at 105°C | % | < 2.5 | 25 |
| 25 | ignition loss (based on the substance dried for 2 hours at 105°C) according to DIN 55 921 | % | 5.5±1.5 | |
| | pH-value (in 5 % aqueous-methanolic suspension) according to DIN 53 200 | | 7.5±1.0 | |
| | conductivity (in 4 % aqueous-methanolic suspension) | μS | < 600 | 30 |
| 30 | bulk density of the unventilated substance according to DIN 53 194 | g/l | 130±40 | |
| | wettability with water | % | < 0.1 | |
| | carbon content | % | 2.5±0.6 | |
| 35 | water uptake at 30°C/30 % relative humidity | % | 1.2±0.4 | 35 |
| | at 30°C/70 % relative humidity | % | 1.5±0.5 | |
2. A hydrophobised precipitated silica as claimed in claim 1 having a drying loss between 2.5 and 0.0 %, a conductivity between 50 and 300 μS and a wettability with water between 0 and 0.05. 40
3. A hydrophobised precipitated silica substantially as described with particular reference to Example 2 or Example 4.
4. A process for producing a hydrophobic precipitated silica as defined in Claim 1, which comprises introducing a hydrophobising agent into an original precipitation suspension of precipitated silica having the following physical-chemical characteristics (characteristics measured after separation from the precipitation suspension, intensive washing with water and long-term drying of the hydrophilic precipitated silica): 45
- | | | | | |
|----|---|-------------------|---------|----|
| | BET-surface according to DIN 66 131 | m ² /g | 160±40 | |
| 50 | average primary particle size from EM photographs | nm | 14-22 | 50 |
| | drying loss according to DIN 55 921 after 2 hours at 105°C | % | 2.5-4.0 | |
| | ignition loss (based on the substance dried for 2 hours at 105°C) according to DIN 55 921 | % | 3.5±1.0 | |
| | pH-value (in 5 % aqueous suspension) according to DIN 53 200 | | 7.0-8.5 | 55 |
| 55 | conductivity (in 4 % aqueous suspension) | μS | < 600 | |
| | bulk density of the unventilated substance according to DIN 53 194 | g/l | 140±40 | |
| | SO ₃ -content (based on the substance dried for 2 hours at 105°C) | % | < 0.3 | |
| | Na ₂ O-content (based on the substance dried for 2 hours at 105°C) | % | < 0.3 | 60 |
- 60 at a pH-value maintained in the alkaline range, stirring the mixture thus obtained, separating off the hydrophobised precipitated silica and subjecting it to long-term drying, after which the product obtained is tempered for 60 to 180 minutes at a temperature of from 200 to 400°C and ground.
5. A process as claimed in claim 4, wherein the product is tempered for 70 to 130 minutes. 65
- 65 6. A process for the production of a hydrophobic precipitated silica substantially as described with

particular reference to Example 2 or Example 4.

7. A hydrophobic precipitated silica when produced by a process as claimed in any of claims 4 to 6.

8. A diorganopolysiloxane-based composition, hardenable to form an elastomer containing a silica as claimed in any of claims 1 to 3 or 7 as a reinforcing filler.

5 9. A one-component silicone rubber joint-sealing compound containing a silica as claimed in any of claims 1 to 3 or 7 as a reinforcing filler.

10. A silicone rubber sheathing compound containing a silica as claimed in any of claims 1 to 3 or 7 as a reinforcing filler

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